抗菌防臭整理剂及其加工方法

本文综述目前使用的有代表性的纤维用抗菌防臭整理剂种类、抗菌机理及其加工方法。

一、目前纤维用抗菌防臭整理剂

目前主要的市售抗菌防臭整理剂如表1所示，其中有道康宁公司的十八烷基二甲基(3-三甲氧基硅烷丙基)氯化铵，ICI公司的聚亚己基双胍盐酸化物，聚氧乙烯三甲基氯化铵，抗菌性"沸石"(载荷银等金属离子的沸石系固体粒子)，以及苯基酮氯化物，3，4，4′-三氯N-碳酰苯胺，1，1′-六亚甲基双[5-(4-氯苯)双胍]二盐酸化物，多氧烷基三烷基氯化铵，含有二价铜盐和硫的导电性聚丙烯腈硫化铜络合物Cu_9S_5 (Digenite)等等。

另外，据最近信息，还有把铜化合物微分散于纤维中的含有导电性硫化铜的纤维素，把铜和锌与羊毛胱氨酸和缩多氨酸相结合的抗菌剂，即使在加热或紫外线照射下也不会产生二噁烷和有害的氯化衍生物的2-羟苯基-2′，4′-二氯苄基醚，把银与阳离子可染涤纶纤维进行离子结合的磺酸银，以及属

表1 最近的抗菌防臭整理剂

类 别	整理剂
无机系列	抗菌性沸石，含有金属离子的可溶性玻璃粉末
在纤维上配位金属的系列	磺酸银，铁酞菁，金属氧化物配位的氨基系聚合物，硫酸锌配位的丙烯酸聚合物
有机硅季铵盐系列	十八烷基二甲基(3-三甲氧基硅烷丙基)氯化铵
季铵盐系列	苯基酮氯化物，十六烷基二甲基苄基氯化铵，聚氧乙烯三甲基氯化铵，聚氧烷基三烷基氯化铵，十八烷基二甲基氯化铵，3-氯-2-羟丙基三甲基氯化铵，N，N-二甲基-N-十六烷基3-(2-磺酸钠乙磺酰基)-丙基溴化铵
胍系列	1，1′-六亚甲基双[5-(4-氯苯)双胍]二盐酸化物，聚六亚甲基双胍盐酸化物
酚系列	烯化双酚钠盐，2-溴-2-硝基-1，3-丙二醇烷基二甲基铵盐，对氯间二甲酚
脂肪酸酯系列	N-硬脂酰-L-谷氨酸钠，十一碳烯酸，甘油脂肪酸酯，丙二醇单脂肪酸酯
铜化合物系列	含有硫化铜的再生纤维素，聚丙烯腈硫化铜络合物，酚系铜螯合树脂
苯酰胺系列	3，4，4′-三氯-N-碳酰苯胺
天然物系列	脱乙酰壳多糖，扁柏硫醇，甲壳质的盐酸盐，氨基糖苷
其他系列	二甲基氨基丙酰胺，P-甲苯磺酸甲酯，碘络合物

表11 调整部温度梯度和用水pH值对缫丝成绩的影响

调整部温度梯度	调整部pH	解舒率(%)	长吐量(kg/件丝)	滞头量(kg/件丝)	吊糸(个/100绪10min)	清洁(分)	糸类(个)	环类(个)
陡梯度	7.0以上	41.5	3.220	6.040	25.5	97.0	14.0	102
	6.0	41.9	2.798	6.366	29.5	97.3	9.4	18.0
	6.0以下	40.0	2.925	6.322	20.2	97.0	11.1	16.6
普通梯度	7.0以上	44.5	3.386	5.960	25.1	97.8	14.4	6.9
	6.0	42.8	3.222	6.080	19.0	97.4	11.0	14.5
	6.0以下	42.0	3.025	6.086	21.4	97.5	8.3	14.5
缓梯度	7.0以上	45.7	3.400	5.720	24.8	97.2	14.3	5.0
	6.0	43.0	3.010	5.850	18.8	98.1	8.6	10.0
	6.0以下	43.0	2.830	5.921	16	98.1	9.6	8.8

如果降低调整部用水的pH值能够有效地抑制丝胶的膨润溶解，就能够建立调整部新的处理技术。因此分析了调整部的温度梯度，pH值和缫丝成绩的关系，其结果的一例如表11所示。

由表可知，pH值愈高，解舒率提高，蛹衣量、环类等减少，但是长吐量、丝故障、绵条类成绩下降。因此，调整部用水的pH值以6.0为中心，呈酸性，可以使调整部的温度梯度变缓进行长时间的高温处理。

(待 续)

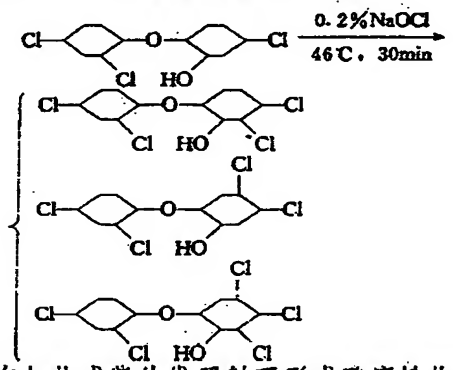
余 雷 章开泰译

于环氧二萜酚酮类化合物的一种扁柏硫醇，具有虾蟹等的甲壳成分的脱乙酰壳多糖，一种由于氨基配糖体抗生物质的氨基葡糖苷等等。

二、目前已被禁用的抗菌防臭整理剂

除了60年代开始使用的有机金属化合物以外，还有如下抗菌防臭整理剂从80年代以来被禁止使用。

TBZ［2-（4-噻唑基）苯并咪唑］有催奇形性害处。2，4，4′-三氯-2′-羟基二苯醚（商品名欧格森DP300）能与氯系漂白剂反应而生成如下三种有毒的氯化衍生物：



并在加热或紫外线照射下形成致癌性物质四氯噁烷，所以约在10年前就不用了。α-溴代月桂醛（BCA）有非常高的异变活性，三（2，3-二溴丙基）磷酸盐（TDBPP）具有异变性和致癌性，对皮肤很敏感。2-（3，5-二甲基吡唑基）-4羟基-6-苯基嘧啶现在也不用于衣料整理了。

三、具有代表性的整理剂及其抗菌机理

1. 无机系列抗菌剂

用 $xM_{2n}O \cdot Al_2O_3 \cdot ySiO_2 \cdot zH_2O$（M为部分或全部用Ag、Cu、Zn等离子置换，n为金属的原子价，x、y、z为系数），这类无机系列抗菌整理剂加工的代表制品，有日本钟纺公司的产品“抗菌性沸石”（商品名BACTEKILLER）。这种制品是利用天然或合成沸石的骨架具有的离子交换性能，载荷以离子键结合的银等金属而制成的“抗菌性沸石”（金属交换量约1%～2%），在涤纶、尼纶等合纤熔融纺的纺丝原液中，混入1%左右而赋予其抗菌性。

这种抗菌剂的急性毒性 LD_{50} 在5g/kg以上，异变性为阴性，对皮肤的刺激性为准阴性，美国环保厅的EPF毒性试验确认，对环境的影响也是安全的。

这种制品的抗菌机理，是由于徐徐溶出的活性氧和银离子扩散入细菌的细胞内，破坏其蛋白质的结构而使其产生代谢障碍。

2. 在纤维上配位金属的系列

用 $[OOC-\langle\rangle-COOCH_2CH_2]_n-$

$OOC-\langle\rangle(SO_3^-Ag^+)-COOCH_2CH_2-$

这类纤维上配位金属系列的抗菌剂整理的代表产品，有日本化药公司的“磺酸银”。这种产品是用后处理法制得的，把含有磺酸基的阳离子可染涤纶织物以浴比1∶5浸渍在0.002%硝酸银溶液中，一边搅拌一边加热至沸，搅拌20min以后冷却，用水洗净并干燥，银离子就与涤纶纤维的可染性残基（$-SO_3^-$）进行离子结合而固着，赋予织物抗菌性。

这种产品的抗菌机理，是由于银离子的电子传导体系破坏了细菌细胞内蛋白质结构（与脱氧核糖核酸反应）而引起的代谢障碍。

3. 有机硅季铵盐系列抗菌剂

用十八烷基二甲基（3-三甲氧基硅烷丙基）氯化铵，这种有机硅季铵盐系抗菌剂整理的制品，有日本东洋纺绩的拜奥赛尔（バイオシル，BIOSIL），它是用道康宁公司的抗菌剂（三甲氧硅烷）丙基十八烷基二甲基氯化铵（商品名DC5700）浸渍或浸轧于棉、尼纶和涤纶等纤维表面而固着的后处理法，使纤维赋予抗菌性。这种抗菌剂具有三甲氧基结合在铵上这样的结构，右侧十八烷基二甲基氯化铵具有杀菌性，左侧的三甲氧硅烷基具有硅烷偶合性。

这个三甲氧基与纤维表面上的羟基进行脱甲醇反应，抗菌剂以共价键固着在纤维上，

同时由于有机硅的接枝聚合，在纤维表面形成薄膜，因此抗菌剂不易从纤维上脱落而保持持久的杀菌效果。

这种抗菌剂的EPF试验，其急毒性LD_{50}为12.27g/kg，对兔子试验未见皮肤刺激性，鱼毒性TL_{50}为56mg/L，其他如亚急性毒性、异变性、催奇形性、粘膜刺激性及袜穿着等试验都是安全的。

这种产品的抗菌机理，是由于季铵盐铵分子的阳离子，静电吸附在微生物细胞表面的阴离子部位，形成的疏水性相互作用，破坏了细胞的表层结构，细胞内物质产生泄漏而停止其呼吸机能，从而使细胞死亡。

4. 季铵盐系列抗菌剂

用聚氧乙烯基三甲基氯化铵，这种季铵盐系抗菌剂整理的代表性产品，有克拉莱公司的SANITER和日清纺绩的佩奇弗莱什（ピ-チフレッシュ，PEACH FRESH）。这种制品用后处理法加工，把脂肪族季铵盐聚氧烷基三烷基氯化铵用反应性树脂固着在纤维（主要是纯涤纶纤维）表面而赋予抗菌性。

这种抗菌剂急毒性LD_{50}为6.51g/kg，对兔子试验未见皮肤刺激性，异变性用Ames法和Escherichia coli试验为阴性，鱼毒性TL_{50}为41mg/L，皮肤贴附性试验为准阴性，安全性很高。

这种产品的抗菌机理，是由于抗菌剂的表面吸附而使微生物的细胞组织发生变化（酶蛋白质和核酸发生变性），细胞质膜引起损伤。

5. 胍系列抗菌剂

用1，1′-六亚甲基双［5-（4-氯苯）双胍］二葡糖酸盐，这种胍系抗菌剂整理的代表性制品，有莱纳翁（レナウン）公司的“通勤快足”，这种产品是把上述抗菌剂加入尼纶等纺丝原液中而赋予抗菌性。由于对纤维的吸附力非常强，耐洗性很好。对细菌有很高的杀菌活性，但对真菌的效果较低。

这种抗菌剂的急性毒性LD_{50}为1～2g/kg，毒性较低，安全性高。对热比较稳定，耐光性稍差。

这种制品的抗菌机理与季铵盐相同，阻碍了细胞溶菌酶的作用，使细胞表层结构变性而破坏。

6. 铜化合物系列抗菌剂

用聚丙烯腈硫化铜络合物，这种铜化合物系抗菌剂整理的代表性产品，有日本蚕毛染色公司的圣达纶—SSN（サンダ-ロン一SSN）和旭化成公司的Asahi BCY。前者是把聚丙烯腈纤维在含有氨和羟胺硫酸盐的2.3%硫酸铜溶液中浸渍后，在100℃下加热120min，再进行还原处理，使氰基和硫化亚铜以配位键进行螯合，形成复杂的配位高分子Cu_9S_5（Digenite），固着在纤维上而赋予抗菌性。这种整理法赋予抗菌性的同时还具有导电性。这种制品非常稳定，耐洗性好，对细菌、真菌都有很强的杀灭力，是一种广谱抗菌剂。

这种抗菌剂急毒性LD_{50}为1.32g/kg，用Escherichia和Sallmonella typhimurium法异变性试验为阴性，用河合法皮肤刺激性试验为准阴性，安全性很高。

后者是在铜氨纤维制造过程中控制脱铜，把铜化合物微分散于纤维中以后，用硫化钾等进行硫化处理，使纤维中含有约15%～20%的硫化铜（CuS、Cu_2S）而赋予抗菌性。这种整理法除抗菌性外，同时还有除臭、导电、阻燃等性能。

这两种制品的抗菌机理，是由于铜离子破坏了微生物的细胞膜，通过细胞膜进入细胞内，与酶的一SH基结合而降低了酶的活性，阻止代谢机能抑制生育而杀灭。

7. 天然物系列抗菌剂

最近，用天然物系抗菌剂整理的抗菌防臭加工制品有所增加，用此类抗菌剂整理的产品，如用脱乙酰壳多糖（β-1，4-多氨基葡糖）整理的制品，有富士纺绩公司的“凯托波莱”（キトポリィ）。用氨基糖苷整理的产品，有福助公司的“清洁自慢”。用扁柏硫醇（4-异丙基-2-羟基-芳庚并-2，4，6-三烯-1-

酮）等的产品。有联合化学工业公司的"UNIKA MCAS-25"及三木理研工业公司的"农霍尔OH留净"（ノンホールOHレヂン）等等。

"凯托波莱"的制法，是把细度在5μm以下的脱乙酰多糖细粉末按纤维素的0.3%～3.0%（w/w）均匀加入波里诺西克（一种高湿模量粘胶纤维）的纺丝原液中，在纤维成形、拉伸以后，均匀分散在再生纤维的组织中而赋予抗菌性。

这种抗菌性的急性毒性LD_{50}为1.5g/kg，由Ames法及Escherichia coli测试的异变性为阴性，由河合用Sump法的开放式粘贴皮肤试验为准阴性，用Draize法皮肤一次刺激性试验和小鼠的亚急性毒性试验均为阴性，安全性很高。

这种制品的抗菌机理，是由季铵化的脱乙酰壳多糖分子的氨基吸附细菌，与细菌细胞壁表面的阴离子相结合，阻碍了它的生化合成机能，从而起到抑制其增殖的效果。也有认为是由于阻止了细菌细胞壁内外物质的输送能力，以及切断了脱乙酰壳多糖的苷键。

"清洁自慢"的制法，是把卡那霉素的羟基用对苯二醛脱氧而成的氨基糖苷，吸附固着在纤维表面而赋予抗菌性。

这种抗菌剂急性毒性LD_{50}在5g/kg以上，对兔子未见皮肤刺激性，鱼毒性TL_{50}为1g/L，由Ames法试验的异变性为阴性，安全性很高。对革兰氏阳性球菌和革兰氏阴性杆菌都有广谱的抗菌效果。

本产品的抗菌机理，是由于这种抗菌剂对细菌的核蛋白体亚单位的30S产生了作用，阻碍了信使核糖核酸（mRNA）的密码子和转移核糖核酸（tRNA）的密码子的相互作用，合成了异常的蛋白质而被杀灭。

联合化学工业公司的"UNIKA MCAS-25"和三木理研工业公司的"农霍尔OH留净"的制法，是把天然扁柏油的扁柏硫醇微胶囊化并制备其3%的乳液树脂，用浸尽法（吸附量70%）处理30min，用100℃以下的温度烘干而赋予纤维抗菌性。有广谱效果，特别对真菌的抗菌力很强。

这种抗菌剂急性毒性LD_{50}为1.119g/kg，皮肤刺激性为准阴性，有很强的广谱抗菌力。这种制品的抗菌机理，是由于使细菌细胞配糖体间氧的螯合作用，以及抗体内蛋白质的变性而被杀灭。

四、抗菌防臭纤维的制造方法

目前抗菌防臭的加工方法，有后处理加工法和原丝改良加工法两大类。从1988年1月至1991年12月的4年间，有关公开了的抗菌防臭加工方法，"特许出愿"有158件，其中后处理加工法117件，原丝改良加工法41件。目前市场上大部分抗菌防臭纤维制品是用后处理加工法制造的，占74%。

1. 后处理加工法

用后处理加工把抗菌剂热固着在纤维上的方法，有喷雾法、浸渍法、浸轧法和涂层法等，一般是在染色整理加工过程中的最后阶段对织物进行这种加工，但也有对已成为产品的织物进行这种加工。

为了提高耐洗性，可以把反应性树脂和纤维交联或者把能形成皮膜的树脂作为媒体，把抗菌剂固着在纤维上。

(1) 用反应性树脂把抗菌剂热固着在纤维表面的方法

这种加工方法，是在抗菌剂成分和纤维交联结合的同时，用反应性树脂把抗菌剂热固着在纤维表面。例如，脱乙酰壳多糖微细粉末季铵盐化了的水溶液中，混入能形成皮膜的树脂，用浸轧法、喷雾法或涂层法加工在尼纶等织物表面，再在130～180℃处理0.5～3min，把抗菌剂热固着。其代表性商品有敷纺公司的"农斯塔科"（ノンスタック），郡山公司的"萨尼泰斯"（サニタイス）等。

(2) 把抗菌剂吸附固着在纤维表面的方法

这种加工方法，是把抗菌剂吸附固着在纤维表面。例如，涤纶制品在染色后的还原

Antibacterial and Deodorant Finishing Agents and the Processing Methods thereof

The categories and antibacterial mechanisms of the representative antibacterial and deodorant finishing agents, which are used at present in fiber, and the processing methods thereof are reviewed in this paper.

1. Antibacterial and Deodorant Finishing Agents Used in Fiber at Present

At the present time, predominant antibacterial and deodorant finishing agents, which are commercially available, are shown in table 1. Those antibacterial and deodorant finishing agents are, for example, octadecyldimethyl(3-trimethoxylsilylpropyl) ammonium chloride (available from Dow-corning Co., Ltd.), polyhexylidene biguanide hydrochloride (available from ICI Co., Ltd.), polyoxyethylene trimethyl ammonium chloride, antibacterial "zeolite" (solid particles of zeolites which load metal ion such as silver and the like), as well as phenone chloride, 3,4,4'-trichloro-N-carbanilide, 1,1'-hexamethano bi[5-(4-chlorobenzol)biguanide] dihydrochloride, polyoxyalkyltrialkyl ammonium chloride, Cu_9S_5 (Digenite) which is an electroconductive complex of polyacrylonitrile copper sulphide containing divalent copper salt and sulfur, and the like.

In addition, according to the latest information, there are many antibacterial and deodorant finishing agents, such as cellulose containing electroconductive copper sulphide which is prepared by dispersing copper compound into the fiber, antibacterial agent in which copper and zinc are combined with lana cystine and polypeptide, 2-oxyphenyl-2',4'-dichlorobenzyl ether which cannot produce dioxane and deleterious chloride derivatives even if it is heated or irradiated by ultraviolet light, silver sulfonate which combines silver and the cationic-dyeable terylene fiber by ionic bond, as well as hinoki thiol belonging to the compounds of tropolones, chitosan having carapace component of shrimp, crab and the like, glucosaminide belonging to antibiotic substance of amino glycoside.

Table 1 Current Antibacterial and Deodorant Finishing Agents

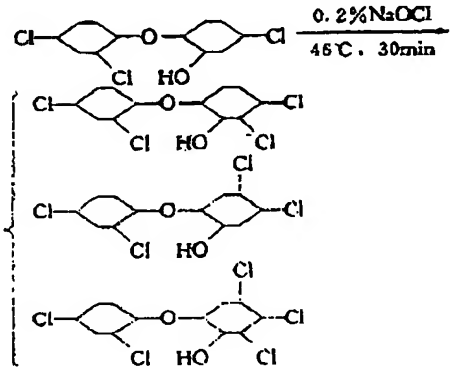
Categories	Finishing agents
Inorganic series	Antibacterial zeolite, soluble glass powder containing metal ions
Series that coordinate metal onto the fiber	Silver sulfonate, iron phthalocyanine, amino polymer in which metal oxide are coordinated, acrylic polymer in which zinc sulfate is coordinated
Organosilicon quaternary ammonium salt series	Octadecyldimethyl(3-trimethoxylsilylpropyl) ammonium chloride
Quaternary ammonium salt series	Phenone chloride, hexadecyldimethylbenzyl chloride, polyoxyvinyltrimethyl ammonium chloride, polyoxyvinyltrialkyl ammonium chloride, octadecyldimethyl ammonium chloride, 3-chloro-2-hydroxylpropyl trimethyl ammonium chloride, N,N-dimethyl-N-hexadecyl-3-(2-sodium sulfate ethyl sulfonyl)-propyl ammonium bromide

Guanidine series	1,1'-hexamethanobi[5-(4-chlorobenzene)biguanide]dihydrochloride, polyhexamethano biguanide hydrochloride
Phenol series	Alkylene sodium bisphenolate, 2-brom-2-nitro-1,3-propyleneglycolalkyldimethyl ammonium salt, parachlormetaxylenol
Fatty acid ester series	Silver N-stearyl-L-glutamine, undecylenic acid, glycerin fatty acid ester, propylene glycol fatty acid monoester
Copper compound series	Regenerated cellulose containing copper sulphide, polyacrylonitrile copper sulphide complex, phenols copper chelating resin
Benzamide series	3,4,4'-trichloro-N-carbanilide
Natural product series	Chitosan, hinoki thiol, hydrochlorate of chitin, glucosaminide
Other series	Dimethylaminopropionamide, P-methyl toluenesulfonate, iodine complex

2. Antibacterial and Deodorant Finishing Agents which are prohibited to use

Besides the organometallic compounds which were used since 1960s, the following antibacterial and deodorant finishing agents have been prohibited to use since 1980s.

TBZ[2-(4-thiazolyl) benzimidazole] is an injurant to cause abnormality. 2,4,4'-trichloro-2'-hydroxy diphenyl ether (tradename referred as Akesson DP300) can react with bleacher of chlorine series into three kinds of toxic chloride derivatives as follow:



and the cancerogenous substance, tetrachloro oxane, can be formed when heated or irradiated by ultraviolet light, so it has not been used any more since ten years. α-bromolauricaldehyde (BCA) has very strong variablity, tri(2,3-dibromopropyl)phosphate (TDBPP) has variability and oncogenicity, and it is very sensitive to skin. At present, 2-(3,5-dimethylpyrazolyl)-4-hydroxy-6-phenylpyrimidine also has not been used in finishing the clothing material any more.

3. Representative Finishing Agents and the Antibacterial Mechanism thereof

1 Antibacterial Agents of Inorganic Series

The representative products which are processed by antibacterial finishing agents of inorganic series, $xM_{2n}O{\cdot}Al_2O_3{\cdot}ySiO_2{\cdot}zH_2O$ (where M may be partially or fully substituted by ions of Ag, Cu, Zn, and the like, and n is atomic value of the metal, x, y and z are coefficients, respectively) comprise "antibacterial zeolite" (tradename is BACTEKILLER, available from Kinebo Co., Ltd. Japan). This product is an "antibacterial zeolite" which is prepared by using the

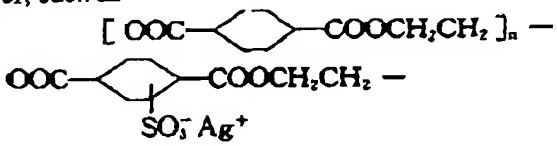
ion-exchange property of skeleton of natural or synthetic zeolite, and loading metal, such as silver and the like, which is combined by ionic bond (with the amount of metal exchanged of about 1% to 2%). The germ resistance is conferred by adding about 1% of said antibacterial agent to the oleo stock of synthon-fusion spinning of terylene, nylon and the like.

Acute toxicity LD_{50} of this kind of antibacterial agent is above 5g/kg, with negative variability and quasi-negative pungency to skin. The results of EPF toxicity testing performed by Environment Protection Agency of America confirm that the environmental impact of this antibacterial agent is also safe.

The antibacterial mechanism of this kind of product is that the active oxygen and silver ion which are dissolved out gradually from the product are diffused into the cell of bacterium to destroy the structure of its protein, thereby to cause dysbolismus.

2 The Series that coordinate metal onto the fiber

The representative products which are processed by antibacterial agents that coordinate metal onto the fiber, such as



, comprise "silver sulfonate" (available from Chemical Drug Co., Ltd. Japan). This product is prepared by post-treating. Cationic-dyeable terylene fabric containing sulfonic group are dipped into solution of 0.002% silver nitrate in the bath ratio of 1:5, then the resulting solution is stirred and heated until boiling, cooled after being stirred for another 20 min, and the fabric is washed by water and dried, thereby silver ion are combined with dyeable residue ($-SO_3^-$) of terylene fiber by ionic bond, and the germ resistance is conferred to the fabric.

The antibacterial mechanism of this product is that the electron conduction system of silver ion destroys protein structure within the cell of the bacteria (reacted with deoxyribonucleic acid), thereby to cause dysbolismus.

3 Antibacterial Agents of Organosilicon Quaternary Ammonium Salt Series

The products which are processed by antibacterial agents of organosilicon quaternary ammonium salt series, such as octadecyldimethyl(3-trimethoxylsilylpropyl) ammonium chloride, comprise BIOSIL (バイオシル) (available from Toyobo Co., Ltd. Japan) which is prepared by the posttreatment of fixing the (trimethoxylsilyl)propyloctadecyldimethyl ammonium chloride (with tradename of DC5700) (available from Dow Corning Co.) onto the surface of fiber of cotton, nylon and terylene by dipping or padding the fiber into the antibacterial agent, thereby the germ resistance is conferred to the fiber. This antibacterial agent has the structure of trimethoxy group bonded to ammonium, octadecyldimethyl ammonium chloride on the right side has germ resistance, and trimethoxylsily group in the left side has coupling ability of silicane.

This trimethoxy group is reacted with the hydroxy group which is located on the surface of the fiber to remove methanol. The antibacterial agent is fixed onto the fiber by covalent bond. At the same time thin film is formed on the surface of the fiber due to the graft polymerization of organosilicon, thus the antibacterial agent will not easily drop off from the fiber in order to remain the permanent germ resistant effect.

In the EPF test of this antibacterial agent, the acute toxicity LD_{50} is 12.27 g/kg, the pungency to skin is not found in rabbit test, and the toxicity to fish TL_{50} is 56 mg/L. Other tests, such as tests

of sub-acute toxicity, variability, abnormality, mucous membrane irritability and socks-wearability and the like, are all secure.

The antibacterial mechanism of this product is that a hydrophobic interaction which is formed by the captions of quaternary ammonium salt molecule absorbing on the site of anion of surface of microorganism cell by static electricity destroys the surface structure of the cell, therefore the leaking of the intracellular substance stops the respiratory function, thereby to make the cell die.

4 Antibacterial Agents of Quaternary Ammonium Salt Series

The representative products which are processed by antibacterial agent of quaternary ammonium salt series, such as polyoxyvinyltrimethyl ammonium chloride, comprise SANITER (available from Clara Co., Ltd.) and PEACH FRESH (ピーチフレッシュ) (available from Nisshinbo Co., Ltd.). Those products are processed by posttreatment of fixing aliphatic quaternary ammonium salt, such as polyoxyalkyltrialkyl ammonium chloride, onto surface of the fiber (primarily pure terylene fiber) with reactive resin, thus the germ resistance is conferred to the fiber.

The acute toxicity LD_{50} of this kind of antibacterial agent is 6 51 g/ kg, the pungency to skin is not found in rabbit test, the variability test is negative using the method of Ames with *Escherichia coli*, the toxicity to fish TL_{50} is 41 mg/L, and the skin adhesivity test is quasi-negative. The security thereof is very high.

The antibacterial mechanism of those products is that the changes of the cell tissues of microorganism (enzyme protein and nucleic acid are denaturalized) caused by the surface adsorption of antibacterial agent result in the damage of the cytoplasmic membrane.

5 Antibacterial Agents of Guanidine Series

The representative products which are processed by the antibacterial agents of guanidine series, such as 1,1'-hexamethanobi[5-(4-chlorobenzene)biguanide]digluconate (also referred as gluconic chlorohexidine), comprise "迅勤快足"(available from Leneum (レナウン) Co., Ltd. Japan). This product is conferred germ resistance by adding such antibacterial agent into spinning oleo stock of nylon or the like. Since the antibacterial agent has very strong adsorbability for fiber, the washablility of it is excellent. The product has excellent germicidal activity for bacterium, but has little effect on fungus.

The acute toxicity LD_{50} of this antibacterial agent is within the range of 1 to 2 g/kg, the toxicity is low, and security is high. The antibacterial agent is thermostable, but its photostability is relatively poor.

The antibacterial mechanism of this product is the same as that of the quaternary ammonium salt. The antibacterial agent hinders the function of the cell lysozyme, to denaturalize and destroy the surface structure of cell.

6 Antibacterial Agents of Copper Compound Series

The representative products which are processed by antibacterial agents of copper compound series, such as polyacrylonitrile copper sulfide complex, comprise 圣达纶-SSN (サンダーロン-SSN) (available from Sanmo Co., Ltd. Japan) and Asahi BCY(available from Asahikasei Co., Ltd. Japan). The germ resistance is conferred to the former product by dipping polyacrylonitrile fiber into 2.3% copper sulphate solution containing ammonia and hydroxylamine sulfate and then heating at 100℃ for 120 min, followed by reduction treatment to chelate cyan group with cuprous sulfide by coordination bond to form complicated coordinate polymer Cu_9S_5 (Digenite) which is

fixed onto the fiber. Not only germ resistance but also electroconductivity can be conferred by this treatment method. This product is very stable with good washability and very strong germicidal activity for bacterium and fungus, which is a broad-spectrum antibacterial agent.

The acute toxicity LD_{50} of this kind of antibacterial agent is 1.32 g/kg, the variability is negative in the *Escherichia* and *Sallmonella typhimurium* tests, and the pungency to skin is negative in 河合 test. The security thereof is very high.

The germ resistance is conferred to the latter product by controlling the decopperization during preparation of the copper ammonia fiber, and dispersing the copper compound into the fiber, then sulphidizing with potassium sulfide and the like, to make the fiber contain about 15% to 20% copper sulphide (both CuS and Cu_2S). Besides germ resistance, deodorization, electric conduction, flame retardance and the like are also conferred by this treatment method.

The antibacterial mechanism of such two products is that because copper ion destroys the cell membrane of the microorganism and enters into cell through cell membrane, then combine with -SH group of enzyme and reduce the enzyme activity, the metabolism function of the cell is interdicted and its generation is inhibited, thereby the microorganism is killed.

7 Antibacterial Agents of Natural Product Series

Recently, the antibacterial and deodorant products which are processed by antibacterial agents of natural product series are increasing. The products processed by such antibacterial agents comprise "凯托波莱" (キトポリ) (available from Fuji Spinning Co., Ltd.) processed by chitosan (β-1,4-polyaminoglucose), "清洁自悦" (available from Igawara Co., Ltd.) processed by aminoglucoside, "UNIKA MCAS-25" (available from Joint Chemical Industrial Co., Ltd. (联合化学工业公司)) and "农霍尔OH宙净"(ノンホルOHレヂン) (available from Mikiriken Co., Ltd.) processed by hinoki thiol (4-isopropyl-2-hydroxy- cyclohepta-2,4,6-triene-1-ketone).

The preparation method of "凯托波莱" is that the fine powder of deacetylating polysaccharide which has the degree of fineness of below 5 μm is added into spinning oleo stock of polynosic (a kind of high wet modulus viscose fiber) in the ratio of 0.3% to 3.0% (w/w) of cellulose, and homodispersed into the tissue of the regenerated fiber after the fiber is formed and stretched, thereby the germ resistance is conferred to the fiber.

The acute toxicity LD_{50} of this antibacterial agent is 1.5g/kg, the variability thereof is negative using the method of Ames with *Escherichia coli*, and the open skin-sticking test is quasi-negative by 河合 with Sump method. The single pungency to skin is negative in Draize test, and the sub-acute toxicity is also negative in rat test. Therefore the security of the product is very high.

The antibacterial mechanism of this product is that the amino group of quaternized chitosan molecular absorbs bacterium, and combines with the anion on the surface of the cell wall of the bacterium, thereby to hinder the function of the biochemical synthesis and inhibit its proliferation. It is also considered that the ability of transporting the substance inside and outside of cell wall of bacterium is inhibited and the glycoside linkage of chitosan is cleaved.

The preparation method of "清洁自悦" is that the hydroxy of kanamycin is deoxided with phthalaldehyde into aminoside, which is then absorbed and fixed onto surface of fiber, thereby the germ resistance is conferred to the fiber.

The acute toxicity LD_{50} of this kind of antibacterial agent is above 5 g/kg, and the pungency to skin is not found in rabbit test. The toxicity to fish TL_{50} is 1 g/L, the variability is negative using the method of Ames. The security thereof is very high. This antibacterial agent is

broad-spectrum antibacterial agent for both gram-positive cocci and gram-negative bacillus.

The antibacterial mechanism of this product is that this antibacterial agent effects on 30S of ribosomal subunit of bacterium, and hinders interaction between codons of messenger RNA (mRNA) and codons of transfer RNA (tRNA), and synthesizes abnormal proteins, thereby the bacterium is killed.

The preparation method of "UNIKA MCAS-25" (available from Joint Chemical Industrial Co., Ltd) and "农霍尔 OH 雷净" (available from Mikiriken Co., Ltd.) is that the hinoki thiol of natural hinoki oil is microencapsulated, and 3% emulsion resin thereof is prepared, then the resulting material is treated for 30 min by absorbing method (the adsorptive capacity is 70%), then dried at the temperature of less than 100℃, thereby the germ resistance is conferred to the fiber. These products have broad-spectrum effect, in particular, they have very strong germicidal activity for the fungus.

The acute toxicity LD_{50} of this kind of antibacterial agent is 1.119 g/kg. The pungency to skin is quasi-negative. These products have very strong broad-spectrum germicidal activity. The antibacterial mechanism of these products is that the bacterium is killed due to chelation of the oxygen between glycosides of bacterium cell and denaturalization of the protein in the antibody.